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RESEARCH STUDIES ON THE DISSEMINATION OF SOLID AND LIQUID AGENTS

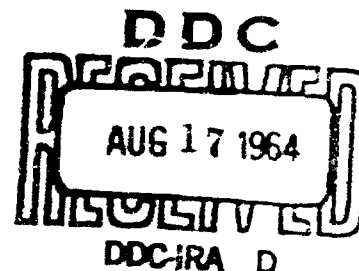
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July 7, 1964

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ABSTRACT

Current status is discussed of a research program designed to provide fundamental information regarding the processes involved in the dissemination of chemical agents. The scope and direction of the program are described. Specific subject areas covered are: (1) Explosive, thermal, ultrasonic and electrostatic aerosol production processes, (2) material treatment by encapsulation and coating techniques, (3) aerosol degradation by pyrolytic, oxidative, hydrolytic, pyrolytic and combustion processes.

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I INTRODUCTION

The objective of this research program is to provide fundamental information for long range over-all modernization of dissemination techniques. The program is planned as a study of the basic physical and chemical processes involved in the dissemination of liquid and solid materials to produce particles and droplets, and the further interaction of energy with the particles to produce an effective cloud of the desired agent. Key problems involved are energy coupling mechanisms and their efficiencies, possible material degradation processes, and mechanisms controlling particle size and concentrations. Initially the program has been divided according to the following outline.

1. Aerosol Production

- | | |
|---------------|------------------|
| a. Explosive | d. Electrostatic |
| b. Thermal | e. Atomization |
| c. Ultrasonic | f. Natural |
| | g. Condensation |

2. Material Characteristics and Treatment

- | | |
|------------------|--------------------------|
| a. Encapsulation | c. Inter-particle forces |
| b. Coatings | |

3. Aerosol Degradation

- | | |
|----------------------------|--------------------------|
| a. Agglomeration | d. Oxidation - Reduction |
| b. Ignition - Deflagration | e. Hydrolysis |
| c. Pyrolysis | |

4. Assessment

Critical evaluation of the literature is the first goal of this program. This is expected to be the principal effort during the first 6 to 8 months of the program and will culminate in a major report on the state of knowledge of dissemination processes and recommendations regarding the most fruitful research directions. Problem analyses and preliminary experiments to establish limits and to delineate fruitful approaches are being undertaken as soon as it seems profitable and logical to do so.

Experiments in some areas have already begun. In other areas which require more thorough literature reviews and analyses, experiments will begin later. Similarly, all the topics listed above will not be pursued concurrently, but it is planned that all of them will be included in the course of the program.

The following senior investigators are responsible for the indicated phases of the program and contributed to this quarterly report.

George R. Abrahamson	- Explosive Processes
Lionel A. Dickinson	- Thermal Processes
Vincent Salmon	- Ultrasonic Processes
Elmer Robinson	- Natural Processes
Charles E. Lapple	- Electrostatic Processes
Arthur G. Brown	- Microencapsulation
Paul L. Magill Metronics Associates, Inc.	- Powder and Slurry Aerosolization Characteristics
Theodore Mill	- Oxidative and Pyrolytic Processes
Robert C. Robbins	- Hydrolytic and Condensation Processes
Willis A. Rosser	- Droplet Ignition Processes
Majorie W. Evans	- Deflagration Processes
William C. Thuman	- Coordination of Assessment Procedures

Over-all technical supervision and administrative support is provided by Ilia G. Poppoff and William C. Thuman

II RESEARCH ACTIVITIES AND PLANS

A. Explosive Processes

1. Plan of Investigation

The explosive dissemination problem has been divided into the following problem areas:

- (1) shock effects prior to breakup of the case
 - a. brittle case
 - b. ductile case

- (2) ejection of the agent from the case
 - a. flow of liquid agents through line orifices
 - b. solid agents
- (3) expansion of the agent into a cloud
 - a. single particles
 - b. clouds of particles
- (4) upper bounds on performance
- (5) present performance

The objective of the first three problem areas is to determine the important processes and parameters involved; the objective of the last two is to place upper and lower bounds on performance.

The lower bound will be based on the efficiency obtainable with present devices and thus will depend heavily on past work. In seeking an upper bound, the approach will be to devise analytical models which give a lower bound on the energy-absorption mechanisms of the explosive dispersal process. For example, four energy-absorbing mechanisms which must be contended with are: (1) the surface energy of the droplets, (2) the breakup of the case, (3) the work required to project the particles to their desired final position, and (4) the energy absorbed in the blast wave.

2. Review of Past Work

The review of past work has consisted of a literature review, attendance at the Fifth Coordination Seminar on Chemical and Biological Dissemination Research, and a visit to CRDL.

Reports by government contractors dealing with the subject have been ordered from the Army Chemical Center. References to these reports were obtained from bibliographies prepared by William Thuman during his visit to the Army Chemical Center. An additional 86 reports of interest were found from Defense Documentation Center bibliographies. Of these 86 reports, 18 were determined to be pertinent by the examination of microfilm copies of the documents at the DDC Office in Sunnyvale.

The open literature has been searched by an examination of Chemical Abstracts, Physical Abstracts, Dissertation Abstracts, and The Applied Mechanics Review. In addition, several bibliographies on the subject have been examined, primarily one on the Explosive Dissemination of a Liquid (June 1963) prepared by William Lai.

A large number of documents have been obtained and are currently being evaluated.

3. Plans for Next Quarter

In the coming quarter four lines of investigation will be pursued: (1) continuation of literature review, (2) shock effects prior to breakup of the case, (3) upper bound with particle motion and the blast wave as the energy-absorbing mechanisms, and (4) performance of present systems.

B. Thermal Processes

1. Pyrotechnic Studies

New concepts of pyrotechnic formulation are being studied to improve the survival chances of the agent in contact with the hot oxidizing flame formed by the oxidant and the fuel comprising the pyrotechnic. It is planned initially to study the effectiveness of the procedures selected by burning mixtures in the "in vitro apparatus" now being developed for kinetic studies.

The existing computer program for thermochemical properties of propellants is now in the course of modification to include the combustion products of typical pyrotechnics.

2. Supersonic Injection Studies

The use of secondary injection to atomize liquids in a supersonic gas stream has been studied using a rocket motor as the source of the gas. The range of experimental parameters investigated is shown in Table I. Formulations of propellants used for these tests are given in Table II. Most of the initial tests were concerned with developing the necessary hardware and determining the capabilities of the method for injection of either liquids or solids. Both were successfully

Table I

TEST PARAMETERS FOR ATOMIZATION IN SUPERSONIC GAS STREAMS

Chamber Pressure psi	Test No.	Propellant Type	Burning Time sec	Propellant Flow Rate, w_f , lb/sec	Fluid Injection Rate, w_i , lb/sec	Fluid Injected
		(PBAN)				
1000	1	111	2.0	3.695	3.728	Water
1050	2	111	2.1	3.665	8.183	Water
1000	3	111	2.1	3.875	6.055	Water
1400	4	111	2.0	4.098	5.567	Water - 97% Soap - 3%
1400	5	111	2.0	4.144	7.328	Water - 94% Soap - 6%
1400	6	111	1.9	4.058	6.322	Water - 58% Carbon - 42%
1400	7	111	2.3	4.188	3.903	Water/red dye
1150	8	111	3.0	1.853	3.72	Water
1600	9	103	3.6	2.556	6.111	Water - 70% Sugar - 30%
1050	10	175	1.01	4.525	5.713	Water
950	11	175	1.08	4.167	4.565	Water
1000	12	175	1.05	4.324	5.486	Water - 80% Glycerine - 20%
1200	13	175	0.90	5.000	8.689	Water
1100	14	175	0.95	4.674	7.189	Water - 80% Glycerine - 20%
1200	15	175	0.90	5.122	6.478	Water - 80% Glycerine - 20%
1300	16	175	0.92	5.674	6.033	Water - 80% Glycerine - 20%
1250	17	175	0.97	5.330	6.196	Water - 80% Glycerine - 20%
1200	18	175	1.0	5.230	5.920	Water
1150 (av.)	19	175	≈1.0	5.240	6.200	Water

Table II

PROPELLANT FORMULATIONS

	PBAN 111	PBAN 103	PBAN 175
Ammonium Perchlorate	78	80	
Potassium Perchlorate			78
PBAN Terpolymer Binder*	20	20	20
Thermax Carbon			2
Iron Oxide	2		
Burning Rate at 1000 psi, in/sec	0.5	0.3	0.95

*Polybutadiene-acrylic acid-acrylonitrile = PBAN

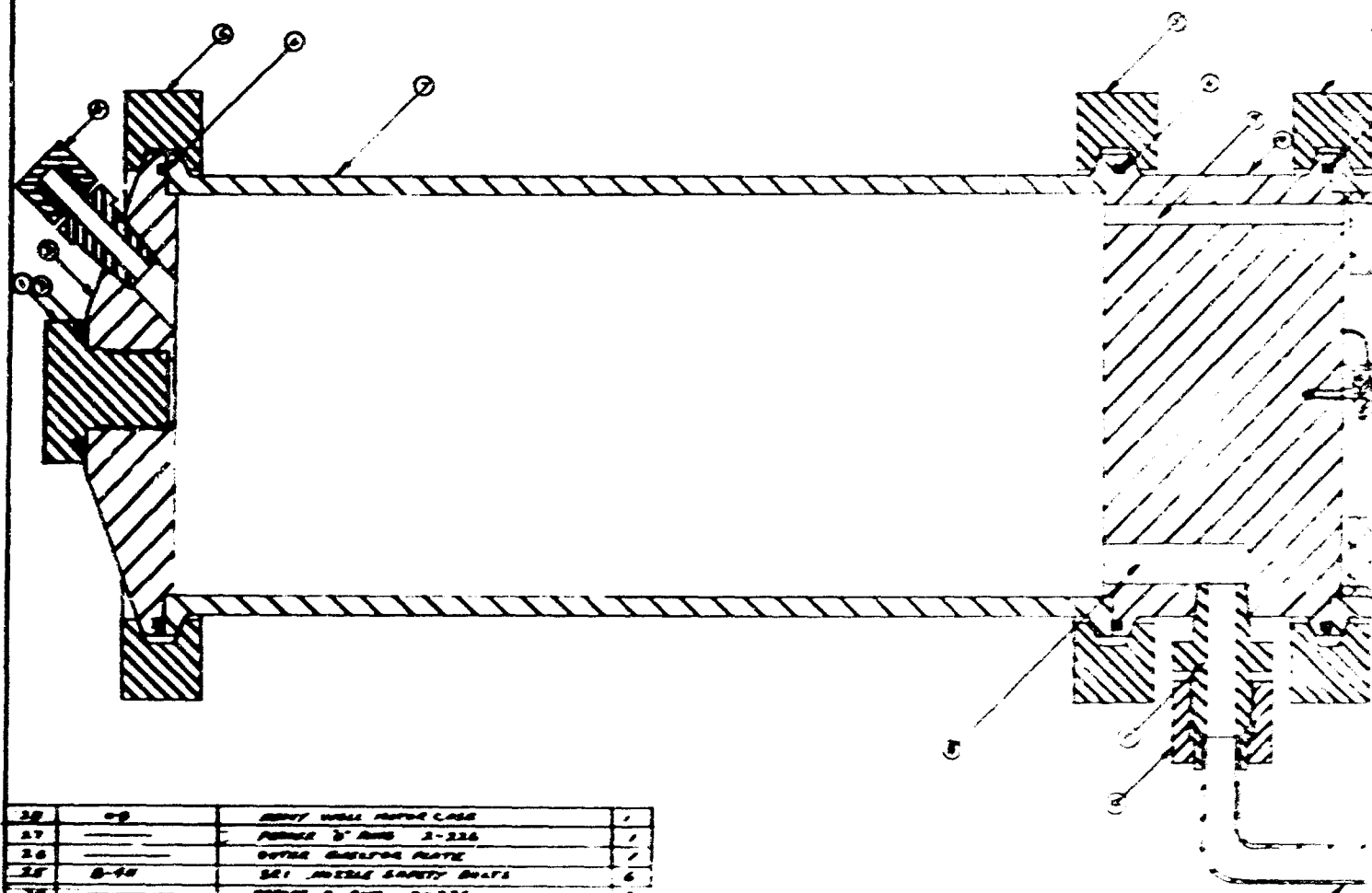
dispersed when the solids (carbon) were gelled in a liquid. A suspension containing 42% carbon in a water gel was injected and atomized at a solids rate of 2.65 lb/sec. Liquids were atomized at rates to 8.90 lb/sec.

In its present state of development the supersonic atomizer is a self-contained, portable device shown in Fig. 1. Combustion gas is bled from the 5-inch-diameter rocket motor chamber to pressurize the tank containing the agent. The fluid flows into the exit portion of the rocket nozzle where gas expansion gives velocities in the range of 6000 ft/sec. The gas temperature at the injection orifices is approximately 1000°K.

In another investigation of the potential area of coverage of the supersonic atomizer, the device was mounted to allow rotation like a pin-wheel with the exhaust jet providing the necessary thrust. The experimental spin table ready for field testing is pictured in Fig. 2. The aerosol dispersion produced (Fig. 3) covered an initial circular area (before wind drift) larger than 50 yards in diameter with an action time of less than 3 seconds.

C. Ultrasonic Processes

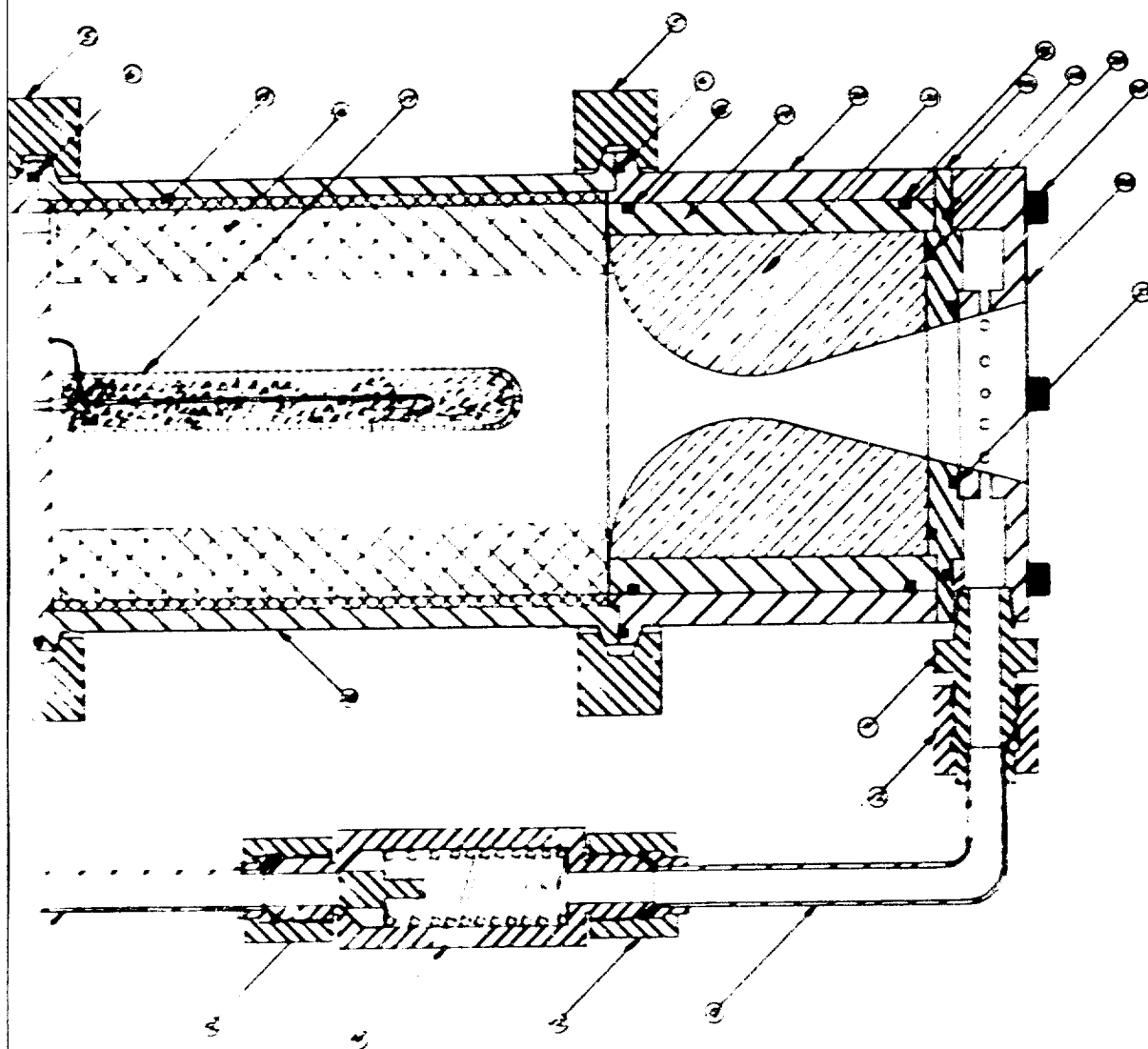
The use of sonic energy for generating and modifying aerosols and dispersion of fine particles is being studied, particularly the energy



ITEM	S/N AND NUMBER	DESCRIPTION	QTY
28	0-0	ROCKET WALL MOTOR CASE	1
27		PISTON 5" DIA 2-226	1
26		OUTER BURNER PLATE	1
25	B-98	S/L INSIDE SAFETY SHAFT	6
24		PISTON 5" DIA 2-226	1
23		PISTON 5" DIA 2-226	1
22		INNER BURNER PLATE	1
21	B-98	COMPOSITE INSIDE INSERT	1
20	C-98	INSIDE BURNER	1
19	B-98	INSIDE INSERT BURNER	1
18		PISTON 5" DIA 2-226	2
17		S/L INSIDE SAFETY SHAFT	1
16		PISTON 5" DIA 2-226	1
15		PISTON 5" DIA 2-226	1
14		PISTON 5" DIA 2-226	1
13		PISTON 5" DIA 2-226	1
12		PISTON 5" DIA 2-226	1
11		PISTON 5" DIA 2-226	1
10		PISTON 5" DIA 2-226	1
9		PISTON 5" DIA 2-226	1
8		PISTON 5" DIA 2-226	1
7	C-9	PISTON 5" DIA 2-226	1
6	B-98	PISTON 5" DIA 2-226	1
5		PISTON 5" DIA 2-226	1
4	C-98	PISTON 5" DIA 2-226	1
3		PISTON 5" DIA 2-226	1
2	B-98	PISTON 5" DIA 2-226	1
1		PISTON 5" DIA 2-226	1

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FIG. 1 SCHEMATIC DIAGRAM OF



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STANFORD RESEARCH INSTITUTE		6-529	
MEMO PARK, CALIF.			
PROJECT NO. 1-101		SUBJECT: DISPERSED BY UNIT	
DATE: 1-1-52		DRAWN BY: [illegible]	
CHECKED BY: [illegible]		APPROVED BY: [illegible]	
DESIGNED BY: [illegible]		TESTED BY: [illegible]	
ANALYZED BY: [illegible]		CALCULATED BY: [illegible]	
CONSTRUCTED BY: [illegible]		ASSEMBLED BY: [illegible]	

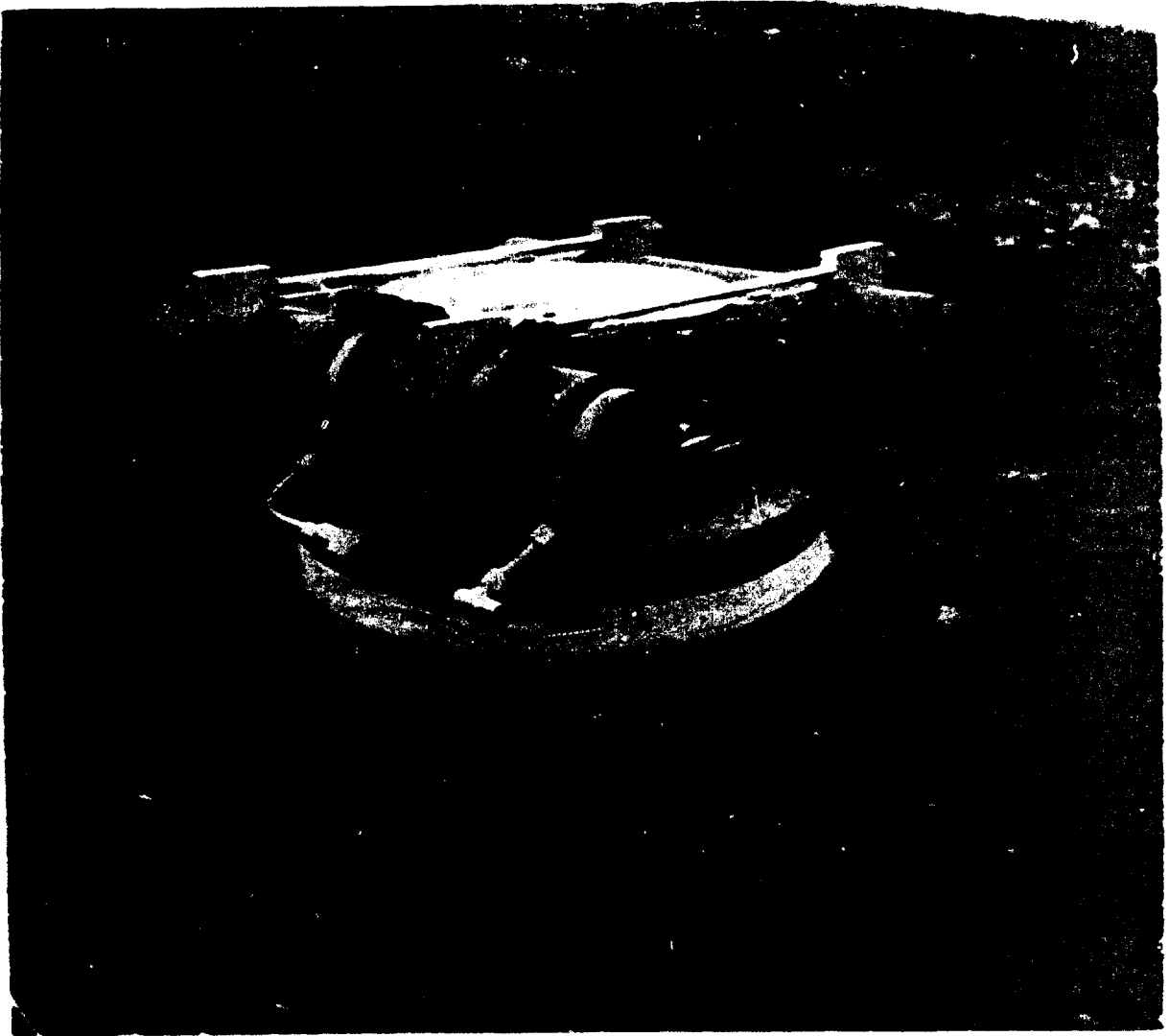


FIG. 2 EXPERIMENTAL ROCKET MOTOR SPIN DISSEMINATOR



FIG. 3 CLOUD PRODUCED BY ROCKET MOTOR SPIN DISSEMINATOR

required and the particle parameters of the resulting cloud. The sonic techniques to be considered are:

- a. Use of high-pressure, high-frequency pulsations in an atomizing nozzle supply pressure to produce uniform particles
- b. Sonic vaporization of liquids from a surface vibrating with high acceleration, or from the focal region of a focused sonic radiator
- c. Interaction of intense air-borne sound with a cloud of particles.

1. Literature Search

The literature search has been completed on:

- a. Means of producing fog from a liquid by sonic vibration
- b. Sonically aided dispersion of aerosols
- c. Theoretical and experimental work on mechanisms for fog production and methods of analysis and measurement.

A total of 685 unclassified references and abstracts has been compiled and is presently being reviewed. A number of pertinent papers have been collected and are being studied to avoid duplication of effort now and in the future. Little information is available on production of particles by high-frequency pulsations of supply pressure to an atomizing nozzle. The yield of usable cards on this topic was approximately 50 percent; 125 were provided by the DDC branch at Sunnyvale, California.

The bulk of the reviewed literature deals with the mechanism of fog and particle production as functions of frequency and intensity. Although the purpose is to correlate the two parameters with particle size, and in some cases with particle concentration, the properties of the liquid being atomized are seldom correlated with the sonic production of vapor. Improvement and/or modification of the system is likewise seldom considered, although the transducers used are usually inefficient for the application. The transducer-environment coupling mechanism therefore seems a natural point of departure for research in the production of sonic fog. A list of pertinent articles that may exist in the classified literature has been requested, and partially received, from DDC Sunnyvale.

The following general conclusions may be drawn from the literature search:

- a. Research on fast evaporation methods for liquids into air and dispersion of solids into clouds has been extensively done in the USSR and allied countries. Approximately 80 to 85 percent of the unclassified entries in sonically aided evaporation and theoretical work on particles suspended in a sonic field are Russian.
- b. The same situation exists for the entries related to techniques for evaluation of sonic fields in the measurement of particle cross sections, size, distribution, etc.
- c. Approximately 10 percent of the entries provided by DDC are related to ultrasonic applications. This small fraction suggests that reports supplied to the DDC are not up to date in the field of ultrasonic interaction with aerosols and ultrasonically aided diffusion of liquids into a gas.

2. Experimental Work

Three experimental sonic vaporization generators using a concentrator ("horn") attached to the transducer have been constructed in the SRI shops. The commercially available generators are low-frequency devices (up to 45 Kcps) such as those used in sonic drilling, and do not appear able to produce small particle fog ($< 4\mu$ particle size). Frequencies in the 100 to 1000 Kcps range are needed. The cost involved in manufacturing experimental sonic concentrators outside the Institute is quite high and does not appear justified at this time. A technique for machining the concentrators shape which will produce optimum concentration has been developed, and uses a standard lathe and a rotating tool bit arm. The sonic concentrators thus produced will be bonded to barium titanate transducers properly backed by a second metallic mass. Size and shape of the concentrator are determined by the frequency and degree of amplification desired; at present there is no adequate theory of the action of solid concentrators. Optimization must thus be accomplished empirically by successive changes in size and shape of the

backing-transducer-concentrator system. For accelerating the optimization process, the use of analogs has been tried -- with generally poor results. Here, a pool of Hg was set to replace the backing of a transducer-concentrator system. Proper backing thickness was achieved by adding or extracting Hg. It was possible with this method to optimize thickness, but the final vibrational amplitude of the concentrator was but a fraction of that obtained with a backless transducer-concentrator thickness. Solid backing was also tried and similar results were obtained.

A review of these results and the theories used to explain vibrational phenomena in these concentrators discloses two points of interest that will be studied in future work.

- a. The theory for the vibrational system under development (i.e., that of driver system and vibration concentrator) is an extension into high frequencies (60 Kcps and up) of the theory that describes low-frequency systems (45 Kcps and lower). The theory for low-frequency systems has received much attention because of the use of LF systems in sonic drilling, soldering, welding, etc. At frequencies higher than about 60 Kcps it is extremely difficult to cause "piston-like" vibration (i.e., that in which the transducer surface moves uniformly up and down and where all the points on the active surface exhibit the same in-phase displacement). The phenomena have been discussed in detail in the literature. The limitations posed by this action are to be investigated.
- b. In view of the previous discussion, an alternative design approach must be developed. For this, a more complete knowledge of the behavior of solid high-frequency vibrating systems must be evolved. Much of this has been done to date at SRI, but definitive experiments are still necessary (e.g., a complete mapping of the surface vibration of a transducer-born system; study of the ρc (characteristic impedance) matching between transducer and born; optimization of the geometrical and intrinsic parameters, etc.).

A suitable probe is being constructed for mapping a vibrating transducer-horn system. This probe must be sensitive to both the magnitude and direction of the vibration. Construction of the probe is well under way. Construction of two 60 Kcps horns (concentrators) has been completed; these are presently under test. A set of holes, 4 to 25 mil in diameter, has been drilled in the high-amplitude region of one of the horns. Water is injected into the lower end of the holes and, when the system is vibrating in resonance, a spray of water droplets is generated. These two transducer-horn systems will be analyzed with the vibration pickup (now under construction) and a vector map of the vibration will be drawn.

The optical system which will be used to record and evaluate test results is being constructed. A concrete table (for rigidity) has been completed and the components of the system are being assembled on it. Electronic apparatus for producing short pulses of light at known times is in the design and experimental construction stage.

D. Natural Processes

Two topics have been pursued during this period -- wind-blown dust dispersion processes and dissemination processes for certain pollen and spores. The analysis of wind-blown dust mechanisms has been carried out through a study of the literature. The studies of the characteristics of pollen and spores has included both a literature review and some exploratory laboratory experiments.

1. Wind-blown Dust Mechanisms

The characteristics of wind-blown dust dispersions have been described by Bagnold in his book¹ in 1941 and expanded upon in later papers.² The investigations of Bagnold seem to be able to account for the characteristics of dust clouds on the basis of the particle size distribution and wind conditions.

¹Bagnold, R. A., The Physics of Blown Sand and Desert Dunes. Methuen, London, 1941

²Bagnold, R. A., The re-entrainment of settled dust, Int. J. Air Poll. 2, 357-363, 1960

The extensive "dust bowl" type clouds are due to the presence of both large (diameter $> 80\mu$) and small (diameter $< 50\mu$) grains in the surface soil. The small grains are dislodged by the action of wind-driven large grains. Once they are dislodged the turbulent wind will keep them in suspension, and they can be carried for long distances and to high altitudes. If the surface dust is composed only of small particles, no air-borne suspension is expected even with strong winds because impacts of large particles are needed to drive the small particles through the stagnant protective air layer at the surface. If the surface dust is composed only of large grains, wind will cause them to move by saltation as a low cloud. The top of the cloud is no higher than would be expected from the bouncing movements of the grains and seldom is observed to exceed shoulder height.²

Bagnold's explanations for the characteristics of dust clouds have been generally substantiated by Chepil³, who also carried out field experiments and wind tunnel tests of dust movement. At the present time there does not seem to be any reason to plan an experimental program to study wind-blown dust.

2. Pollen and Spore Characteristics

The study of dissemination characteristics of pollen and spores has been concerned with whether some natural materials such as lycopodium or puffball spores are especially easy to disperse as an aerosol of unagglomerated particles. The literature references studied so far have not been concerned with this aspect of pollen and spore dissemination. One study of puffball dissemination has shown that large numbers of spores can be expelled by the impact of a rain drop on the outside of the puffball.⁴ No information was given, however, on whether the spores were expelled as single particles or as agglomerates.

Preliminary experiments with lycopodium and with glass beads indicate that agglomerates are formed by the lycopodium but not by the glass beads. The number of agglomerates formed by the lycopodium spores could be reduced by increasing the amount of energy used to disseminate a given weight of material.

²Chepil, W. S., Dynamics of wind erosion: I. Nature of movement of soil by wind. Soil Science 60, 305-320 (1945)

⁴Lilly, V. G. and H. L. Barnett, Physiology of the Fungi, McGraw-Hill, New York, 1951, p. 350.

3. Plans for Next Quarter

The research program in the coming quarter will mostly be concerned with further experiments with puffball dissemination processes.

Plans are presently being made to obtain some growing puffballs for more careful study. Experiments carried out so far with dried samples show that puffball spores are usually found with a number of spores connected to a single fiber, and then the fibers are matted together to form flocculated particles. The spores are held quite strongly to the fibers and no successful method of separation has been found so far.

E. Electrostatic Processes

During the quarter the literature search has been essentially completed. This search has yielded some 600 to 700 references that are believed to be directly pertinent. At first, some 300 to 400 references had been obtained from Chemical Abstracts, Battelle Review, STAR, and private files. During the past month, it was found that Physical Abstracts contained many references that were missed by Chemical Abstracts. This is the source of the additional references. It is expected that some 30 references to reports on government projects will be obtained. Some of these are in hand; others will be procured as soon as possible.

Since it will be impossible to critically analyze all the references found within the allotted funds, it is proposed to pick out those most relevant for this purpose (say 100). Additional references will be reviewed only as subsequent evaluations might dictate. Analytical effort in this direction has started.

F. Microencapsulation

During this initial quarter of the project the activities of the microencapsulation group have been concerned primarily with orientation towards the materials and needs of CRDL to provide a background for a systematic study of the roles which microencapsulation might play in solution of dissemination problems. Experimental efforts directed toward

the production of a wide range of encapsulated materials for use in the studies have also been initiated.

In addition, of continuing interest is a critical review of all known encapsulation methods, their state-of-the-art capabilities and limitations, and their potential for further development. A bibliography is being accumulated as a basis for a later comprehensive report. It appears pertinent to provide a brief summary at this time of the various microencapsulation methods with which we will be mostly concerned.

1. Encapsulation Methods

The following methods are those with which we have had the most experience from previous studies. Discussion of them is not meant to be a comprehensive summary of the literature in this field. In general, these methods employ systems in which the wall-forming liquid phase is in thermodynamic equilibrium with the liquid dispersion medium so that ample time is available for optimum wall development in contrast to dynamic encapsulation methods in which perfection of the wall may or may not be complete. These methods are mostly covered by patents of The National Cash Register Company. Four generic methods with a large number of possible variations in technique are involved.

a. Gelatin Method

This method involves formation of a coacervate liquid, concentrated in polymer, by interaction of high isoelectric point gelatin with a negative colloid(s) or by salting-out or by lyotropic agents. The coacervate spreads around the dispersed phase particles (or droplets) or a dispersion of finely divided solids in liquid droplets to accomplish encapsulation. The "gelatin" film or wall so formed is then hardened and the capsules isolated and dried by any one of several procedures.

Almost any liquid or solid having a solubility in water of 0.1% or less can be encapsulated by this process or by one of its many modifications. Permeability of the capsule wall can be varied widely, depending somewhat on the internal phase, and may be as low as a few

percent per year. Typical "internal phases" might be hydrocarbons, fats and oils, plasticizers, complex organic sulfides, and a wide range of water-insoluble solids. Polar liquids, if reasonably insoluble in water can often be encapsulated by this method, but wall permeability will often be high, and the internal phase only poorly retained. Post-treatments for improving retention are often possible, however.

A variety of terms are used to describe modifications in procedures. The coacervation region may be entered by change in pH or in temperature, or by dilution. There may be advantages in passing through the liquid coacervate region quickly ("quick-drop") or slowly (slow cool). A single negative colloid may be employed ("2-way") or several negative colloids may be used together or in sequence ("3-way;" "3-1/2 way," etc.). Other hydrophilic colloids than gelatin may also be used, and the polymer may be preformed or polymerized in situ. Interfacial polymerization may be employed to modify wall properties or to assist in encapsulating reactive internal phases, and other methods for modifying wall properties also exist, including possibilities for producing "leaky" or "controlled release" capsules.

Capsule sizes can be varied from a few microns to several millimeters and the percent internal phase from perhaps 20 to 95%. Each new internal phase may require some modification of basic techniques, especially in the extremes of capsule size, wall thickness and permeability, and internal phase solubility, viscosity, density and interfacial tension.

b. Exchange Methods

In this approach gelatin microcapsules containing toluene or similar internal phase are produced first. These capsules are then treated with successive batches of the liquid desired as internal phase. Under the right conditions of capsule formation and subsequent treatment, exchange can occur in a few hours or less. Retention can often be very good with suitable post-treatment. Typical liquids encapsulated in this way include dioxane, ethyl alcohol, or solutions based on these liquids.

c. Phase Separation

In this group of methods organic solvent media are used to produce capsule walls from solvent-soluble synthetic or natural polymers. As in the aqueous gelatin methods the encapsulation depends on formation of a second, polymer-rich, phase which will spread around and enclose each particle of the dispersed material which it is desired to encapsulate. Phase separation is based on addition of a second polymer solution to a solution of the polymer which is to be used as wall material. If solvents and solubility parameters of the polymers have been chosen correctly and proper procedures based on a knowledge of the phase diagrams for the system have been used, a concentrated solution of the polymer of interest will "phase out" and can be used for encapsulation -- much as in the gelatin method. Hardening of capsule walls and isolation of capsules depend very much on details of the phase diagram and proper choice of solvents. Chemical crosslinking may also be possible.

The method is especially useful with water-soluble solids, which must of course be insoluble in the organic solvents employed. Wall materials can be varied widely and include ethyl cellulose, cellulose nitrate, polyvinyl chloride, polyvinylidene chloride, Kel-F type polymers, and many others.

These methods are particularly useful for controlled or sustained release of pharmaceutically active materials but very small capsule sizes are more difficult to achieve than with gelatin methods.

d. Polymer Dispersion Method

In this method a liquid medium is employed in which both the wall material and the material to be encapsulated are insoluble. Encapsulation liquid is formed by raising the temperature, and encapsulation follows the usual pattern. Hardening is mostly a matter of decreasing the temperature. Numerous variations of this procedure allow formation of a wide variety of products including water-soluble and water-insoluble materials in fatty or waxy walls or in walls of many thermoplastic polymer compositions.

The method is particularly useful for solid internal phases, for intermediate capsule size, and for thermal release at rather sharp temperatures.

2. Experimental Program

The planned experimental studies in approximate order of priority have been developed as follows.

a. Encapsulation of Liquids and Solids for Pyrotechnic Dissemination

Initial emphasis is on preparation of 100-300 capsules of inactive liquids and solids covering a wide range of vapor pressures, viscosities, flashing characteristics, and other physical properties. Subsequent studies will be concerned with encapsulation of < 10% CS in high density slurry form. Capsules will be provided for studies at CRDL as well as for special pyrotechnic studies to be carried out at SRI. Capsule variables to be studied will include effects of encapsulation method and finishing, wall thickness, and capsule size. Possible ablative roles of the capsule wall will be examined.

b. Sustained Release

Encapsulation should provide possibilities for maintaining active concentrations over an area for predetermined periods of time. Data will be accumulated on release rates for a range of internal phase characteristics for selected encapsulation parameters.

c. Porous Coatings

Coatings which would assure release of liquid agents on cutaneous contact would be desirable, as would porous coatings for controlled time release of volatile agents. Both represent types of "leaky" capsules. To this end, previous studies which indicated possibilities for high permeability walls (conceivably temporarily sealed by secondary thermal release walls) will be explored.

d. Wall Materials Providing Pyrotechnic Fuel

Wall materials providing the major source of fuel for pyrotechnic dissemination -- either in combination with added oxidizer or without requirements for added oxidizer -- should provide possibilities for high active content compositions. Thio-organic polymers might be specially interesting for the first type, nitrocellulose compositions for the second. Both types will be studied in detail.

e. Protection for Photosensitive Agents

Protein agents and possibly other materials which are photosensitive should be protectable by encapsulation in wall materials including blocking or other protective agents. Encapsulation of proteins will be studied using egg albumen as typical internal phase and with efforts directed towards achieving capsules less than 10μ in diameter.

f. Rupture Capsules

Retentive capsules which would release their contents by foot pressure on area penetration would have special advantages and will be explored initially using high detectability inactive materials.

g. Other Approaches

Other special uses of microencapsulated agents will be studied as required by other parts of the total program.

Preparation of encapsulated materials has been started. To date, these include samples of dioctyl phthalate in the 100μ and $< 10\mu$ range. The latter were somewhat aggregated and experiments to decrease this aggregation are under way.

3. Future Work

Major emphasis for the immediate future will be on encapsulation of a wide range of liquids and solids in the $100-300\mu$ range.

G. Powder and Slurry Aerosolization Characteristics

This phase of the program is being carried out by Metronics Associates, Inc., under a subcontract which was initiated June 1, 1964.

1. Program Plan

Initial studies under this investigation are directed toward dry powder aerosolization. For the following reasons experimental work is being conducted initially with selected lots of zinc-cadmium sulfide fluorescent pigment* referred to as FP.

*Manufactured by U.S. Radium Corporation in accordance with specifications provided by Metronics Associates, Inc. Manufacturer's Code Number is USRC 2267.

a. The FP has been used extensively for atmospheric diffusion studies during the last 15 years based on techniques developed here at Metronics. These techniques include empirical methods for aerosolizing the dry pigment under controlled conditions, aerosol sampling procedures, and specialized assessment methods. Among the latter, an empirical laboratory procedure has been established to measure quantitatively the number of particles aerosolized by the standard blower type generator per gram of bulk powder introduced into the generator. These aerosol generator performance tests (AGPT) provide a large body of data which can benefit the current investigation.

b. The FP material is composed of primary particles in the size range of interest viz. 0.5 to 8 μ . Lots can be selected having size distributions which peak below or above 2 μ . In all lots the primary particles appear as agglomerates in the bulk powder. Most agglomerates are loosely held; some may be more tightly held by partial sintering and can be identified at high magnification (800X).

c. Flow properties of the bulk FP material are changed markedly with certain dry additives. Estersil (du Pont) is by far the most effective; however, the exact mechanism by which it acts is not known. With the standard aerosol generator, treated and untreated FP show the same degree of aerosolization, but it is suspected that, with less energy input, differences may be apparent with the treated material showing better aerosolization.

d. The FP material is available in several colors of which four are sufficiently distinctive so that in a mixture each may be separately identified by its characteristic fluorescence when irradiated by UV. Thus membrane filter samples containing a mixture of these four kinds of particles can be assessed microscopically to determine the number present for each color. Accordingly, prepared bulk mixtures of the colored FP can be used to determine the effectiveness of aerosolization procedures by determining the extent to which particles of different colors are separated.

One of the over-all objectives of the dry powder aerosolization program is to determine the energy required for aerosolization and how the

energy may be minimized by dry powder pretreatment. As a first step, it is desirable to establish as reliably as possible the number of primary particles per gram in the bulk powder which may then be used as an index of the degree of aerosolization achieved under given conditions. In the past the particles per gram (ppg) have been determined primarily from AGPT analysis (Item a. above). Although results are reproducible there is a possibility that some grinding, i.e., breakup of primary particles, may be taking place in the high speed blower. Therefore an independent method for determining ppg would be desirable particularly one which has an energy input below that required for fracturing primary particles. Use of liquid suspensions appears to be the most promising and has received first attention.

Apart from the determination of ppg, use of liquid suspension has other advantages in the current program. For example, sedimentation techniques using the Cenco Photolometer or the MSA centrifugation based on Whitby's method provide relatively rapid means for measuring particle size distributions without tedious microscopic sizing. However, all of these methods depend on achieving complete dispersion of the powder in a liquid medium. Therefore, if appropriate methods can be developed for obtaining suspension suitable for ppg determination these methods can also be applied to particle size distribution measurements by an appropriate sedimentation procedure.

2. Research Activities

Two lots of FP 2267 have been used in exploratory tests to determine particles per gram in liquid suspensions. The suspensions were prepared with various dispersal methods using 20 mg of the FP powder in 100 cc of water containing one of three wetting agents. Five cc of the primary suspensions was transferred to 300 cc of water with wetting agent and 5 cc of this secondary suspension was filtered through a 0.45 μ Millipore filter. In some cases two or more filter samples were prepared from the same secondary suspension. Filters were counted at 100X or 200X in accordance with established standard procedures. From the filter count and dilutions used, the number of particles per gram

could be determined for comparison with the number per gram previously measured in the AGPT analysis.

To obtain a more rapid assessment of the suspensions and particularly to determine changes associated with the various wetting agents and dispersion methods, an alternative analytical procedure was used. The primary suspension was placed in a colorimeter tube and exposed to UV light. A small photocell connected to a recording milliammeter measured the fluorescent intensity of the suspended particles at a fixed distance (3 cm) below the liquid surface. Suitable precautions were taken to minimize the effect of UV and stray light on the photocell so that the recorded light intensity-time curves reflected the sedimentation process. Uranine dye solutions were used to check light intensity and fluorometer stability. No attempt has been made as yet to calibrate the fluorometer absolutely since relative values in the slope of the intensity-time curve are sufficient to show changes in the degree of dispersion. For example, the difference between one and three minutes of hand shaking is readily apparent from the curve shape.

Suspensions were prepared with a range of initial dispersion energy including magnetic stirring, ultrasonic (20 and 40 kc), Waring Blender and vigorous action with a syringe. Wetting and dispersing agents include Calgonite, Photoflo, and Marasperse N. Results of six dispersion tests are summarized in Table III.

Agitation with the magnetic stirrer does not provide sufficient energy to break up the aggregates. Substantial improvement was obtained with syringe dispersal as shown in Test No. 6. Good agreement is shown between liquid dispersion and previously measured aerosol dispersion and also between the three separate filter samples run in this test. In Test No. 7 the powder was first wet with aniline then dispersed in alcohol. Dispersion was less complete than in Test No. 6 according to the filter counts and also as indicated by the fluorometer curves.

The need for relatively vigorous initial agitation is evident and further tests will be run using a hand homogenizer in place of the syringe. A larger and more reproducible energy input can be achieved with the homogenizer. Particle size distributions will be made on selected filter samples obtained from the liquid dispersions and aerosol generator.

RESULTS OF DISPERSION TESTS

Dispersion Test No. Serial Dilution	Slide Nos.	FP Material	Dispersion Medium	Dispersion Method	Number of Particles on Filter	Number of Particles per Gram	% of AGFT Count
1	1	2267*	0.10% Calgonite	Stirring Bar	522,000	$.79 \times 10^{10}$	45%
	2	Lot 11-42-2	Calgonite	Stirring Bar	489,000	$.74 \times 10^{10}$	42%
2	3	Lot 11-42-2	Calgonite	Stirring Bar	192,000	1.18×10^{10}	67%
	4	Lot 11-42-2	Calgonite	Stirring Bar	182,000	1.11×10^{10}	63%
3	5	Lot 11-42-2	0.05% Photoflo	Stirring Bar	147,000	2.2×10^{10}	126%
	6	Lot 11-42-2	Photoflo	Stirring Bar	95,000	1.4×10^{10}	80%
4	7	Lot 11-42-2	Photoflo	Stirring Bar	766,000	1.25×10^{10}	71%
	8	Lot 11-42-2	Photoflo	Stirring Bar	633,000	1.03×10^{10}	59%
5	9	2267**	0.05% Photoflo	Stirring Bar	281,000	1.82×10^{10}	110%
	10	Lot 1339-2	0.01% Marasperse N	Stirring Bar	242,000	1.56×10^{10}	94%
6	13	Lot 1239-2	0.01% Marasperse N	Syringe	289,000	1.74×10^{10}	105%
	15	Lot 1339-2	0.01% Marasperse N	Syringe	282,000	1.69×10^{10}	102%
7	16	Lot 1339-2	0.01% Marasperse N	Syringe	284,000	1.71×10^{10}	103%
	17	Lot 1339-2	1.0% Aniline 99% Ethanol	Stirring Bar	266,000	1.60×10^{10}	96%

*The ppg for FP 2267, Lot 11, 42-2 was $1.74 \times 10^{10} + 11\%$

**The ppg for FP 2267, Lot 1339-2 was $1.66 \times 10^{10} + 13\%$

H. Oxidative and Pyrolytic Processes

Degradation of CS and BZ agents during pyrotechnic dissemination is thought to be caused by thermal and/or oxidative reactions of the agent in the thermal layer. Since potential and actual agents have a diversity of chemical structure, and new pyrotechnic devices with differing thermal and/or oxidative characteristics will probably be developed, the only reasonable way of determining the potential degree of degradation for a given agent will be to provide rather specific data concerning thermal and oxidative rates of reaction over a range of temperatures and concentrations. For a given agent these data should permit a reasonable estimate of the yield of a pyrotechnic device, provided time-temperature data are known for the thermal layer.

It is planned, initially, to measure the thermal degradation rate of the present pyrotechnic agent, CS, in a static or flow system. Concurrent with this, estimates will be made of the time-temperature profile of the pyrotechnic system. Coupling of these data should indicate what contribution, if any, thermal degradation makes to the over-all reduction in yield. Oxidative degradation of CS will then be measured over an experimentally feasible range to determine the contribution of oxidation to the degradation process. These results should provide insight on the pyrotechnic degradation process and serve as a guide for estimating degradation of new agents. Experimental procedures are now being developed to measure both oxidative and thermal stability of CS over a range of temperature high enough to overlap the calculated temperature of the thermal layer. These kinds of data should tell us if the assumptions regarding degradation mechanisms are at least qualitatively correct or if some other kind of degradation mechanism is important, e.g. attack by Cl or ClO radicals.

I. Hydrolytic Processes

1. Research Activities

The short-time (millisecond scale) high temperature loss reactions in the dissemination of CW agents can cause serious losses, depending upon agent properties and dissemination conditions. Agent degradation

can occur primarily through oxidation and pyrolysis, or even by hydrolysis.

The possibility of significant agent loss due to hydrolysis in the atmosphere, at ambient temperature, was considered and an assessment is being made. Although as yet we do not have the necessary data to present precise reaction rate information, we have enough liquid hydrolysis data to calculate the order of magnitude of atmospheric hydrolysis of dispersed VX liquid. In this type of system gas-phase diffusion is rapid compared to diffusion in the droplets and a steady state is quickly attained in which water vapor concentration will remain constant. The rate of disappearance of agent is then $-\frac{dA}{dt} = kS$ where S is the total surface area of the aerosol, i.e., the reaction is pseudo-first order with respect to the droplet surface.

$$S \text{ (area of sphere)} = 4\pi r^2 = \frac{3 \times \text{Volume of Sphere}}{r}$$

$$\text{or } S = \frac{3A}{r}$$

$$-\frac{dA}{dt} = k \frac{3A}{r}$$

The work of Callahan and Scott⁵ indicates that the uncatalyzed liquid phase hydrolysis of VX at pH 7 and 25°C proceeds at a rate of approximately 10^{-12} moles $\text{cm}^{-3}\text{sec}^{-1}$. In a typical aerosol the concentration of agent A would be $\sim 10^{-7}$ moles cm^{-3} ; with a radius of one micron and an excess of water vapor ($> 10^{-6}$ moles/cm) we may calculate a very approximate rate constant:

$$-\frac{dA}{dt} = k \frac{3A}{r} \quad 10^{-12} = k \frac{3 \times 10^{-7}}{10^{-4}} \quad k \approx 1/3 \times 10^{-9} \text{ cm sec}^{-1}$$

The calculated half-life based on this special rate constant, with droplets of one-micron radius, is $\approx 2 \times 10^5$ sec or about two days. This is such a long period of time that it must be concluded that ambient temperature hydrolysis of VX can cause only trivial loss of agent in a practical period.

⁵Callahan, J. J. and R. V. Scott. Hydrolysis of VM and VX in Dilute Aqueous Solutions [U]. CWLR 2356, January 1960 (SECRET)

2. Plans

The assessment of possible hydrolytic losses in the dissemination of agents other than VX will continue.

J. Droplet Ignition Processes

An apparatus has been assembled with which to study the ignition of small combustible droplets suddenly exposed to a hot oxidizing atmosphere. The essential elements include a vibrating reed atomizer,⁶ an electrically heated furnace, and a means of measuring droplet size. The atomizer produces a stream of uniformly sized drops which fall through an aperture into the vertical core of the furnace filled with hot oxidizing gas of chosen composition and temperature. A droplet of combustible liquid as it falls through the furnace will evaporate and may ignite if conditions are favorable. The important variables that can be studied include the temperature of the oxidizing atmosphere, the chemical and physical properties of the droplet, the initial size of the droplet, and the size of the droplet at the time of ignition.

A semiquantitative mathematical model describing the ignition of a drop has been derived as a guide for experimental study. The essential features of the model are based on these observations:

a. Freely falling drops suddenly exposed to a hot oxidizing atmosphere do not ignite if the initial drop size is less than a certain value which depends on the temperature and composition of the oxidizing gas.⁷

b. Burning drops are enclosed by a contact surface which is defined by the streamline that separates the oxidizer gases from the combustion products emerging from the droplet flame. Mass transport across the contact surface may occur by diffusion but not by convection. If evaporation is sufficiently rapid, a contact surface will exist in the absence of a flame.

⁶Rayner, A. C. and H. Hurtig, Apparatus for producing drops of uniform size, *Science*, 120, 672 (1954)

⁷Wood, B. J., W. A. Rosser, Jr., and H. Wise, "A Study of Ignition and Combustion of Fuel Droplets," American Petroleum Institute Publication 1722, August 1963.

Mathematical treatment of simpler, but similar, critical combustion phenomena⁸ suggests that the shape and size of the region between the contact surface and the evaporating drop is an important feature affecting droplet ignition. Our treatment of droplet ignition is based on that premise.

A survey and evaluation of published material related to droplet ignition and combustion is also in progress.

K. Deflagration Processes

A literature search for material relating to the initiation and propagation of deflagration waves in aerosol clouds is under way.

Initial experimental plans are now in progress. Background information concerned with combustion of phosphate esters is being obtained to provide a basis for selection of a series of alkyl phosphate esters having similar or predictable relative reactivities and a broad range of physical properties. It is planned that the behaviors of this series of compounds will be examined in aerosol clouds with a variety of deflagration initiation techniques. A simultaneous study of the same compounds in droplet form (as described in J above) will provide valuable information regarding the relative roles of single droplet ignition and cloud deflagration processes in "flashing" phenomena. The role of combustion product gases will also be considered.

L. Condensation Processes

1. Research Activities

An investigation has been initiated of agent nucleation efficiency of condensation nuclei from the combustion of pyrotechnic mixes. Currently, measurements are being made of the numbers of particles formed from agent simulant vapor when it is mixed with the combustion products of a potassium perchlorate pyrotechnic mix.

⁸Frank-Kamenetskii, D. A., Diffusion and Heat Exchange in Chemical Kinetics, trans. by N. Thon, Princeton Univ. Press, Princeton, New Jersey (1955)

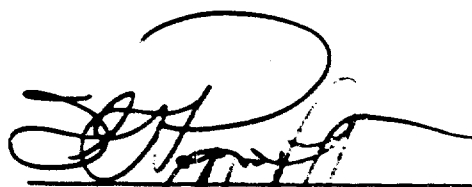
Benzoic acid is the only agent simulant which has been used to date, but the results of the preliminary experiments indicate that the technique has great potential.

2. Plans

The investigation will be enlarged to include a study of several simulants over a range of vapor pressures. Other simulants under consideration are p-dichlorobenzene, naphthalene, and citric acid. The agent CS will be used in the near future and an investigation of BZ is planned.


Pyrotechnic mixes, representing several types will be compared concerning their nucleation efficiencies. These types are:

1. Mixes containing $KClO_4$ and/or $KClO_3$ which are presumed to supply KCl nuclei*
2. Mixes containing aluminum which will provide Al_2O_3 nuclei
3. Mixes producing only carbon nuclei (example: ammonium picrate monopropellant)
4. Mixes theoretically producing only acid nuclei (example: (1) part ammonium picrate, (2) parts ammonium perchlorate).



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Approved:



Charles J. Cook, Director
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Best Available Copy

*Ions are undoubtedly produced in all cases but are not considered important condensation nuclei when compared with the other nuclei produced in these combustion processes.